

UNIVERSITY OF PENNSYLVANIA

**A STUDY OF THE INFLUENCE OF VARIABLES
ON THE STRUCTURE OF ELECTRO-
DEPOSITED COPPER.**

ARTHUR KENNETH GRAHAM

A THESIS IN CHEMISTRY

PRESENTED TO THE FACULTY OF THE GRADUATE SCHOOL IN PARTIAL
FULFILLMENT OF THE REQUIREMENTS FOR THE
DEGREE OF DOCTOR OF PHILOSOPHY.

Philadelphia
1927

A STUDY OF THE INFLUENCE OF VARIABLES
ON THE STRUCTURE OF ELECTRO-
DEPOSITED COPPER.

A THESIS IN CHEMISTRY

PRESENTED TO THE FACULTY OF THE GRADUATE SCHOOL OF THE
UNIVERSITY OF PENNSYLVANIA IN PARTIAL FULFILLMENT
OF THE REQUIREMENTS FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY.

ARTHUR KENNETH GRAHAM

REPRINT FROM
THE TRANSACTIONS OF THE AMERICAN ELECTROCHEMICAL SOCIETY,
VOL. LII, (1927).

Philadelphia
1927



A paper presented at the Keokuk session of the Fifty-second General Meeting of the American Electrochemical Society, on its Northwestern Trip, Sept. 4-21, 1927, Dr. A. W. Burwell in the Chair.

A STUDY OF THE INFLUENCE OF VARIABLES ON THE STRUCTURE OF ELECTRODEPOSITED COPPER¹

By A. KENNETH GRAHAM.²

ABSTRACT.

A study of the variables in the electrodeposition of copper, namely, the influence of the base metal, metal concentration of electrolyte, acid concentration of electrolyte, agitation, current density, temperature, addition agents and the cathode potentials, in conjunction with each of the above variables, was made under uniform conditions, using an acid copper sulfate electrolyte. Their effect upon the structure of the electrodeposited metal was observed, and the relation of cathode polarization to the structure of the deposit was noted. Additional confirmation was obtained of the evidence that the base metal influences the structure of electrodeposited copper. A simple device for maintaining a constant solution level, and a new design of calomel electrode for preventing diffusion of potassium chloride into an electrolyte, were employed.

A review of the literature reveals that a great deal of work³ has been done dealing with the variables in electrodeposition of metals, and their effect upon the structure of the deposits. The

¹ Manuscript received May 17, 1927.

² Chemist, Hanson and Van Winkle Co., Newark, N. J.

³ Zimmerman, Trans. Am. Electrochem. Soc., 3, 245 (1903); Cowper Cowles, Trans. Far. Soc., 1, 215 (1905); Burgess and Watt, Trans. Am. Electrochem. Soc., 9, 229 (1906); Wren and Kern, Trans. Am. Electrochem. Soc., 20, 165 (1911); Bennett, Trans. Am. Electrochem. Soc., 21, 253 (1912); Schwarz, Internatl. Zeit. für Metallg., 7, 124 (1915); Sieverts and Wipplemann, Z. anorg. Chem., 91, 1 (1915), 93, 287 (1916); Blum, Heller, Rawdon, Trans. Am. Electrochem. Soc., 30, 159 (1916); Kern, Trans. Am. Electrochem. Soc., 33, 131 (1918); Blum, Trans. Am. Electrochem. Soc., 36, 213 (1919); Schwarz, Jour. Inst. Metals, 23, 525 (1920); Stager, Helv. Chim. Acta., 3, 584 (1920); Hughes, Jour. Inst. Metals, 23, 526; Hughes, Trans. Am. Electrochem. Soc., 41, 317 (1922); Hughes, Trans. Far. Soc., 17, 442 (1922); Blum, Circular 52, Bureau of Standards.

conditions under which these studies were made, however, vary greatly so that the results of different investigators in many cases are not comparable, and any attempts to draw general conclusions are of questionable value. In addition, it has only recently been recognized that with copper, upon which most work has been done, and, possibly, with other metals the electrodeposited metal is markedly influenced in structure by the structure of the base metal.⁴ This point has been entirely neglected in previous studies, the value of which, therefore, becomes still more doubtful.

In fact, Hughes⁵ while he attempts to generalize on the experimental results already obtained, states that "work so far done has had relation to individual cases, and the results can not be said to have much general application, . . . much must be done before the influence of this or that factor can be said to be known." And Blum and Rawdon⁶ while formulating a simple theory of the probable mechanism of crystal formation in electrodeposition make this significant statement: "Even with so common a metal as copper, upon which so many researches have been published, no single investigation has included the effects of each of the variables under otherwise uniform conditions."

It was therefore decided to carry out a study along the lines indicated above, to study each variable of electrodeposition independently, and, if possible, to observe the cathode potentials during depositions with the hope of showing some relation between these potentials and the structures obtained as suggested by Blum⁷ and Kohlschütter.⁸ In order to be able to include reproduction, the influence of the base metal structure upon the structure of the deposit, as one of the variables, copper was chosen as the base metal and acid copper sulfate solution as the electrolyte.

APPARATUS.

The copper electrolyte was placed in a small Freas water thermostat, which held 34 liters of solution, and the mercury regulator

⁴ Blum and Rawdon, *Trans. Am. Electrochem. Soc.*, **44**, 305 (1923); Graham, *Trans. Am. Electrochem. Soc.*, **44**, 427 (1923).

⁵ Bulletin No. 6, Dept. Scientific and Industrial Research, London (1923).

⁶ *Trans. Am. Electrochem. Soc.*, **44**, 397 (1923).

⁷ Blum, *loc. cit.*

⁸ *Trans. Am. Electrochem. Soc.*, **45**, 229 (1924).

placed directly in the electrolyte. This was done in order to maintain a constant temperature regulation. The temperature variation in all cases was less than 0.15°C . The thermostat was equipped with a lead cooling coil, the metal stirrer was replaced with glass and a wooden support, impregnated with wax, was substituted for the original metal support holding the mercury regulator.

A bakelite panel *P* was designed as an electrode holder (Fig. 1). Two anodes were spaced 15 cm. (6 in.) apart with two cathodes

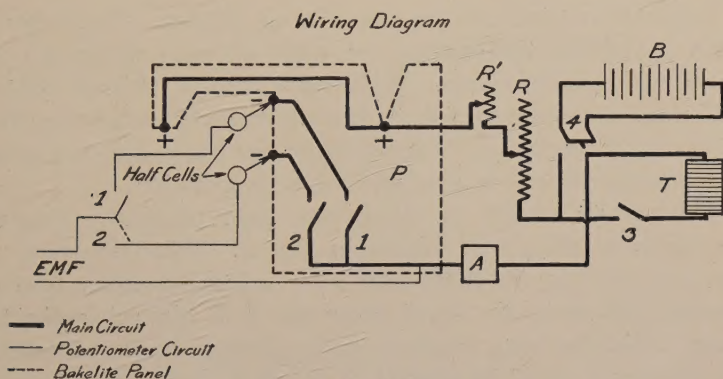


FIG. 1.

placed midway between them. The cathodes were each connected to a switch, 1 and 2, shown in the main circuit of the wiring diagram, by means of which either electrode could be thrown out of circuit when measuring electrode potentials. During dynamic potential measurements only one electrode was left in the circuit at a time, switch 4 was open and 3 closed, the current being supplied from a thermopile T (because of its constant e. m. f.), the resistances R and R' were adjusted to give the proper current density as indicated by the ammeter A , and the two-way switch of the potentiometer circuit thrown in position 1 or 2 as desired. At times other than when potential measurements were being taken switch 3 was open, switch 4 was closed and the current was supplied from storage batteries B .

Chemicals of highest purity were used in preparing the electrolytes. The composition of the baths was checked prior to each

run. The method of analysis used was essentially that described by Blum⁹ for acid copper solutions. The values of specific gravity and concentration were plotted from Blum's table on cross section paper to facilitate reading, and hydrometers which could be read to the fourth decimal place were used. The free sulfuric acid was titrated with normal sodium hydroxide, using methyl orange as an indicator. The accuracy of this titration was better than 0.5 per cent. The possible error in using the hydrometers and reading from the specific gravity-concentration curve was considerably less.

Hughes¹⁰ recommends the use of large volumes of electrolytes for work of this kind, stating that quite different results are obtained with small volumes. With the volume of 34 liters used in this work the concentration of the constituents varied less than 1 per cent during a run. This variation was due to different anode and cathode efficiencies alone and not to evaporation.

The volume of the electrolyte was kept practically constant by means of the device shown in Fig. 2. When the level of the electrolyte in the thermostat went below the outlet tube of the inverted flask, air would enter the flask displacing distilled water, which, in turn, would be siphoned from the test tube into the thermostat until the electrolyte or solution level corresponded to the outlet tube of the flask.

All electrodes consisted of 6 mm. (0.25 in.) copper rod of high purity. Two anodes and two cathodes each of 0.1 sq. dm. (1.6 sq. in.) area were used at one time. Of the two cathodes one consisted of fine grains, the surface of which was buffed to prevent reproduction of the original base metal. It was then cleaned in benzol, alcohol, alkaline cleaner (consisting of Na_2CO_3 , NaOH , and NaCN) and sodium cyanide before plating. The other cathode consisted of metal which had been annealed to give very uniform, large grains in order to produce a marked influence upon the deposited Cu. It was cleaned in benzol, alcohol, alkaline cleaner of the same composition as above, an acid dip consisting of a mixture of sulfuric, nitric and hydrochloric acids and then in sodium cyanide before plating.

⁹ Circular No. 52, Bureau of Standards. See also Scientific Paper No. 275, Bureau of Standards.

¹⁰ Bulletin No. 6, *loc. cit.*

The potential measurements were made with saturated calomel half cells using a Leeds and Northrup, Type K, potentiometer. The half cells were prepared as described by Clark.¹¹

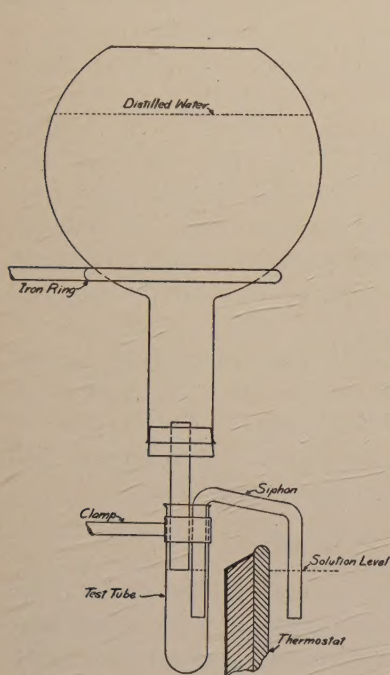


FIG. 2.

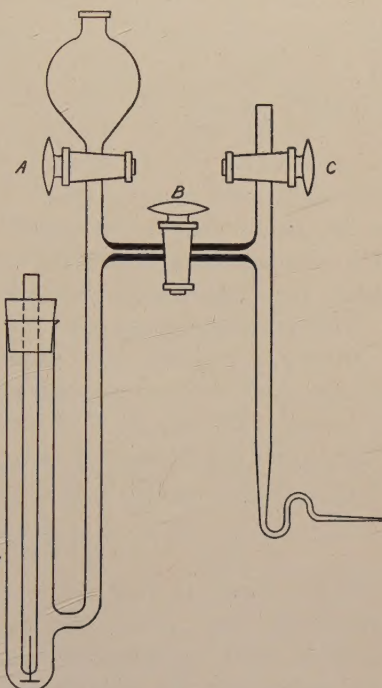


FIG. 3.

The mercury was purified by dropping through a column of mercurous nitrate solution three times. The calomel was prepared by dissolving some of the purified mercury in redistilled nitric acid and then slowly dropping dilute hydrochloric acid, which had been redistilled, into the diluted mercurous nitrate solution with constant stirring. Double distilled water was used throughout, and the c. p. potassium chloride was recrystallized before using.

A new design of electrode was used in these measurements (Fig. 3). After the cell was made up in the usual manner, saturated KCl was added to the bulb at A. By opening the stopcocks at A and B, the arm B was filled with saturated KCl. The

¹¹ Determination of Hydrogen Ions (1923).

stopcock B was not greased so that it could be closed and yet, if wet, would conduct the current. In this way the arm B acted as a saturated KCl bridge.

Before using, with the stopcock B closed and C open, the tip C was washed free of KCl. A pipette was then attached to the top of C by means of a piece of rubber tubing. On placing in the electrolyte the solution was then pipetted up through the stopcock C. Twenty cc. were drawn up in excess of the amount required to fill C. By so doing the KCl solution was completely flushed out back to the stopcock B. The liquid junction was made at this point without contaminating the electrolyte. In addition, if it was desired to renew the liquid junction during a measurement, fresh electrolyte could be pipetted through the stopcock C without removing the cell.

During a run the cells were left in the electrolyte, thereby keeping their temperature constant, but the arm C was kept empty to prevent diffusion of KCl into the solution. Also, a piece of folded filter paper was tied under the stopcock B to prevent KCl from dropping into the acid copper sulfate electrolyte.

VARIABLES STUDIED

In this work the following variables were studied in the order mentioned: base metal, metal concentration of the electrolyte, agitation, acid concentration, current density, temperature, addition agents and the cathode potentials in conjunction with each of the above.

In order to maintain a constant temperature it was necessary to have some agitation of the electrolyte in conjunction with the thermostatic control. The minimum agitation possible, giving the temperature control already stated, was employed in all cases unless otherwise stated. We shall refer to this as standard agitation, and that it was not sufficient to alter noticeably the structure of the deposit is shown later.

Agitation was also necessary to prevent concentration differences throughout the large volume of electrolyte. The results of some unpublished work on nickel electrolytes have shown that the metal concentration in the top and bottom portion of a still plating solution may vary as much as 60 per cent.

STANDARD CONDITIONS

With reference to the variables mentioned the following conditions were adopted as standard and any variation from these conditions are mentioned.

Base metal: The kind of electrodes described above, one set with a buffed surface and another with large grains, unbuffed. In the experimental results the former are the uneven numbered while the latter are the even numbered.

Copper Concentration: 1.5 normal.

Agitation: Standard, as defined.

Sulfuric Acid Concentration: 1.0 normal.

Current Density: 3 amp./sq. dm. (27.9 amp./sq. ft.)

Temperature: 25° C. (77° F.).

Addition Agents: None.

EXPERIMENTAL RESULTS

It is not necessary to dwell upon the influence of the base metal on the structure, since it has already been studied¹², but attention should be called to the fact that even with the buffed surface (uneven numbered figures) the electrodeposit initially reproduces the very fine structure of the buffed surface before taking on the characteristic electrolytic structure. A layer of very fine crystals adjacent to the base metal is visible in each case. This substantiates the claims of the writer¹³ that the electrodeposited copper reproduces the structure of the base metal whatever that structure may be.

EFFECT OF METAL CONCENTRATION.

Reference to Table I and Fig. 4 show that upon increasing the copper sulfate concentration from 0.75 to 1.5 *N* both the static and dynamic potentials became more noble, (polarization decreased) and the size of the crystals increased. At the lower metal concentration and higher polarization the tendency is for the original nuclei or crystals to continue to grow, reproduction is greater, therefore, while at the higher concentration and lower polarization this tendency is reduced.

¹² Blum and Rawdon, *loc. cit.*; Graham, *loc. cit.*

¹³ Graham, Trans. Am. Electrochem. Soc., **44**, 310 (1923).

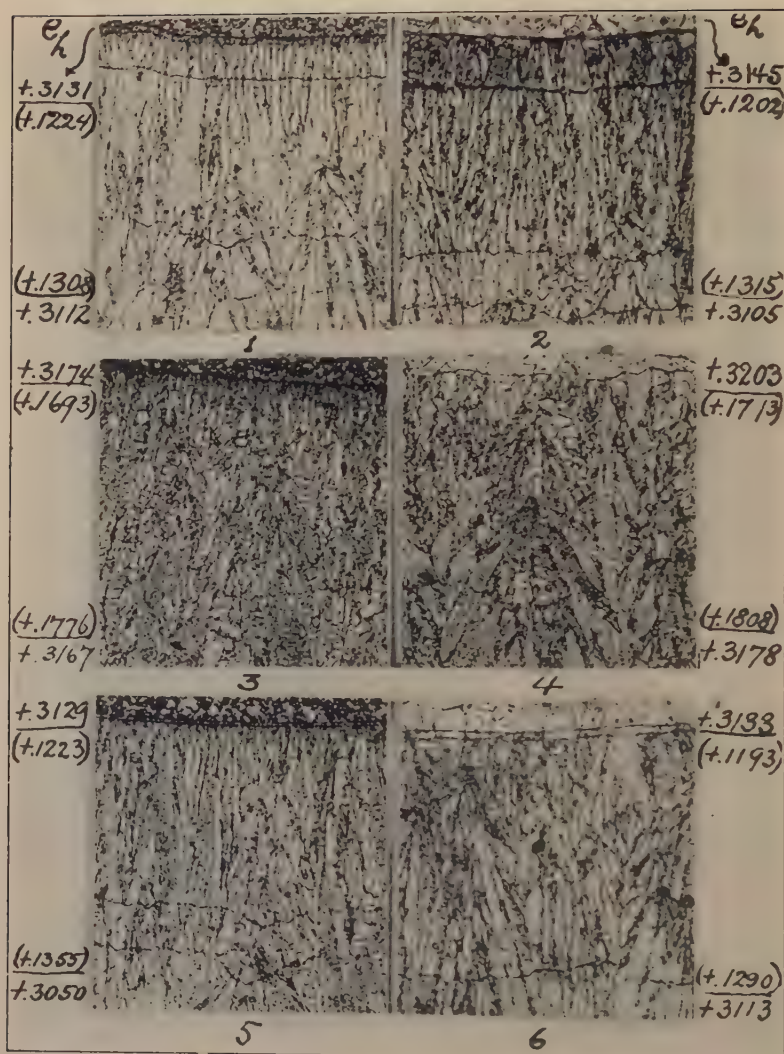


FIG. 4. Effect of Copper Sulfate Concentration.

x 100. Etched with $\text{NH}_4\text{OH} + \text{H}_2\text{O}_2$.

C. D. 1.0 amp./sq. dm.

Temp. 25°C . H_2SO_4 N

No. 1 and No. 2, 0.75 N Cu

No. 3 and No. 4, 1.50 N Cu

No. 5 and No. 6, 0.75 N Cu; less agitation

Values in parentheses are the dynamic potentials; the others the static.

The current density had to be reduced from the standard value to 1 amp./sq. dm. (9.3 amp./sq. ft.) because at the lower concentration of copper (0.75 *N*) the cathode potentials were too irregular with higher current densities. This was probably due to hydrogen evolution, as the acid concentration was normal and the metal concentration low.

EFFECT OF AGITATION.

Reference to Table II and Fig. 4 shows that when the standard agitation required to maintain the temperature control was reduced,

TABLE I.

Effect of CuSO₄ Concentration on Cathode Polarization and Structure in Copper Deposition.

Standard conditions, except current density 1 amp./sq. dm. (9.3 amp./sq. ft.).

Fig. No.	Spec. No.	Variable: CuSO ₄ N	Initial Cathode Polarization Volts	Structure
4	1	0.75	0.1907	Columnar, conical
4	3	1.50	0.1481	Conical, twinned
4	2	0.75	0.1943	Columnar, conical
4	4	1.50	0.1490	Conical, twinned

TABLE II.

Effect of "Standard Agitation" Employed on Cathode Polarization and Structure in Copper Deposition.

Standard conditions, except CuSO₄ = 0.75 *N*; C. D. = 1 amp./sq. dm. (9.3 amp./sq. ft.).

Fig. No.	Spec. No.	Variable: Agitation	Initial Cathode Polarization Volts	Structure
4	1	Standard	0.1907	Columnar, conical
4	5	Reduced	0.1904	Columnar, conical
4	2	Standard	0.1943	Columnar, conical
4	6	Reduced	0.1940	Columnar, conical

no noticeable difference in structure was produced. (Current density, 1 amp./sq. dm.; 9.3 amp./sq. ft.) The potentials also differed only slightly. This means that the uniform agitation employed throughout these runs was not of sufficient magnitude to alter the

structure. That agitation does affect the structure is well known, but the amount used in this work was not sufficient to produce an appreciable effect.

The reduction of agitation was accomplished by fitting a rubber membrane, open at the bottom, around the electrodes. In this way the temperature control and concentration of the electrolyte were unaffected.

EFFECT OF ACID CONCENTRATION.

Acid concentrations of 0.5 *N*, 1.0 *N* and 1.5 *N* were used. Reference to Table III and Fig. 5 will show that with 1.0 *N* sulfuric

TABLE III.

Effect of H₂SO₄ Concentration on Cathode Polarization and Structure in Copper Deposition.

Standard conditions.

Fig. No.	Spec. No.	Variable: H ₂ SO ₄ <i>N</i>	Initial Cathode Polarization Volts	Structure
5	7	0.5	0.0999	Twinned, broken (fine)
5	9	1.0	0.1936	Conical, twinned
5	11	1.5	0.1341	Broken (fine)
5	8	0.5	0.1006	Twinned, broken (fine)
5	10	1.0	0.2005	Conical, twinned
5	12	1.5	0.1395	Broken (fine)

acid the dynamic cathode potentials were less noble (higher polarization) than at either 0.5 *N* or 1.5 *N* acid. On the other hand, the structures were much finer grained in the latter two cases where the polarization was really less and the influence of the base metal reduced. With increased concentration of sulfuric acid the common ion effect and viscosity would increase, which according to Blum should increase the tendency for nuclei formation and the cathode potential difference. No explanation of this is offered at this time.

EFFECT OF CURRENT DENSITY.

Variation of current density is known to produce greater changes in structure and polarization than any other one variable. We found such to be the case. Reference to Table IV and Fig. 6 and



FIG. 5. Effect of Sulfuric Acid Concentration.

x 100. Etched with $\text{NH}_4\text{OH} + \text{H}_2\text{O}_2$.

C. D. 3 amp./sq. dm.

Temp. 25° C.

 CuSO_4 1.5 NNo. 7 and No. 8, 0.5 N H_2SO_4 No. 9 and No. 10, 1.0 N H_2SO_4 No. 11 and No. 12, 1.5 N H_2SO_4

Values in parentheses are the dynamic potentials.

7 will show that as the current density increases, the cathode potential becomes less noble (polarization increases), the structure be-

TABLE IV.

Effect of Current Density on Cathode Polarization and Structure in Copper Deposition.

Standard conditions, except excess agitation on spec. 17, 19, 18 and 20.

Fig. No.	Spec. No.	Variable: C. D. Amp./sq. dm.	Initial Cathode Polarization Volts	Structure
6	13	1.0	0.1481	Conical, twinned
6	15	3.0	0.1936	Conical, twinned
6	17	6.0	*	Treed, conical (coarse)
7	19	9.0	*	Treed, broken (fine)
6	14	1.0	0.1490	Conical, twinned
6	16	3.0	0.2005	Conical, twinned
6	18	6.0	*	Treed, conical (coarse)
7	20	9.0	*	Treed, broken (fine)

* Irregular due to hydrogen evolution.

comes coarser, the tendency to form trees appears, and the influence of the base metal is greatly diminished. At high densities, 6 and 9 amp./sq. dm. (55.7 and 83.6 amp./sq. ft.), it was impossible to make dynamic potential measurements, the irregularity being due to hydrogen evolution. It was also necessary to increase the agitation at these higher current values.

EFFECT OF TEMPERATURE.

Temperatures of 15, 25 and 35° C. (59, 77 and 95° F.) were studied. The dynamic potentials, Table V and Fig. 8, became more noble (polarization decreased) as the temperature increased. With this decrease in polarization the nuclei formation, which was very great at 15° C. (59° F.) diminished greatly so that at 35° C. (95° F.) the structure obtained resembled rolled metal more than electrolytic. The influence of the base metal increases with the temperature.

EFFECT OF ADDITION AGENTS.

When 7.5 g./L. (1 oz./ gal.) of pure $\text{Al}_2(\text{SO}_4)_3 \cdot 16\text{H}_2\text{O}$ were added to the standard copper electrolyte the dynamic cathode

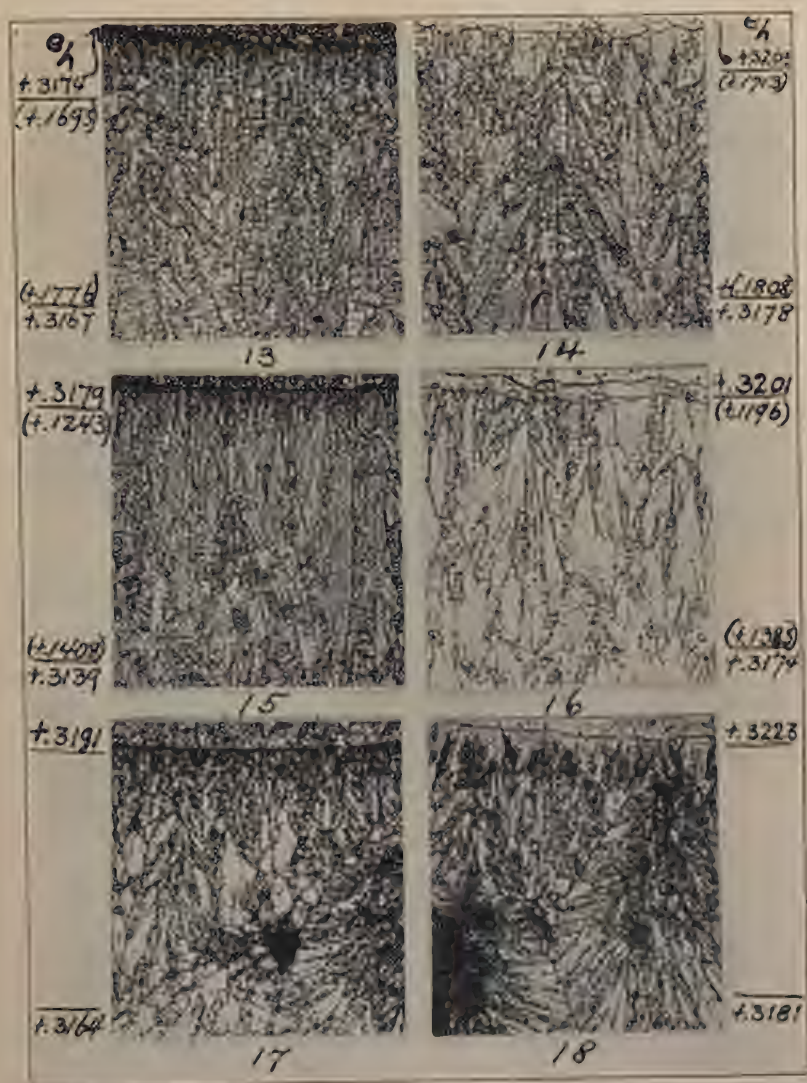


FIG. 6. Effect of Current Density.

x 100. Etched with $\text{NH}_4\text{OH} + \text{H}_2\text{O}_2$.Temp. 25°C . CuSO_4 1.5 N H_2SO_4 1.0 N

C. D.: No. 13 and No. 14, 1 amp./sq. dm.

No. 15 and No. 16, 3 amp./sq. dm.

No. 17 and No. 18*, 6 amp./sq. dm.

* Compare with No. 19 and No. 20 in Fig. 7.

potentials became more noble (polarization decreased) with the resultant increase in nuclei formation and treed deposit. The influence of the base metal was greatly diminished. See Table VI and Fig. 6 and 7.

With an addition of 0.02 g./L. (0.003 oz./gal.) of gelatine to an electrolyte consisting of 1.5 *N* CuSO_4 and 1.5 *N* H_2SO_4 the cathode potential became less noble (polarization increased) as would be expected. (See Table VII and Fig. 9.) The peculiar structure adjacent to the base metal in 31 and 32 can be explained only on the basis that the gelatine migrated to the cathode and was co-deposited with the metal. There is probably a critical con-

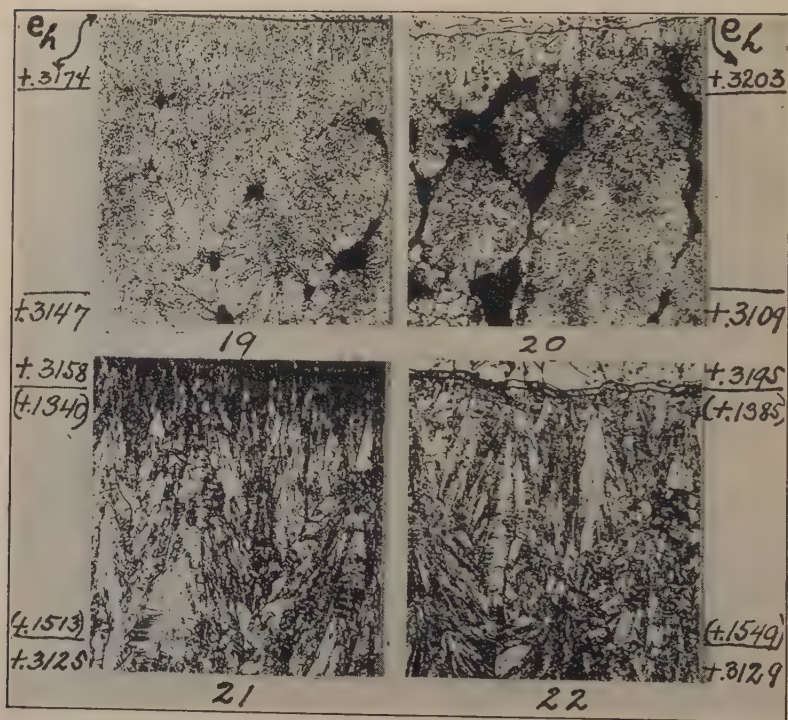


FIG. 7. Effect of Current Density and of Aluminum Sulfate.
x 100. Etched with $\text{NH}_4\text{OH} + \text{H}_2\text{O}_2$.

Temp. 25° C.
 CuSO_4 1.5 *N*
 H_2SO_4 1.0 *N*

No. 19 and No. 20, 9 amp./sq. dm.*
No. 21 and No. 22, 3 amp./sq. dm.
with 7.5 g./L. $\text{Al}_2(\text{SO}_4)_3 \cdot 16\text{H}_2\text{O}^\dagger$

* Compare Fig. 6, No. 17 and No. 18. $\dagger$ Compare Fig. 6, No. 15 and No. 16.

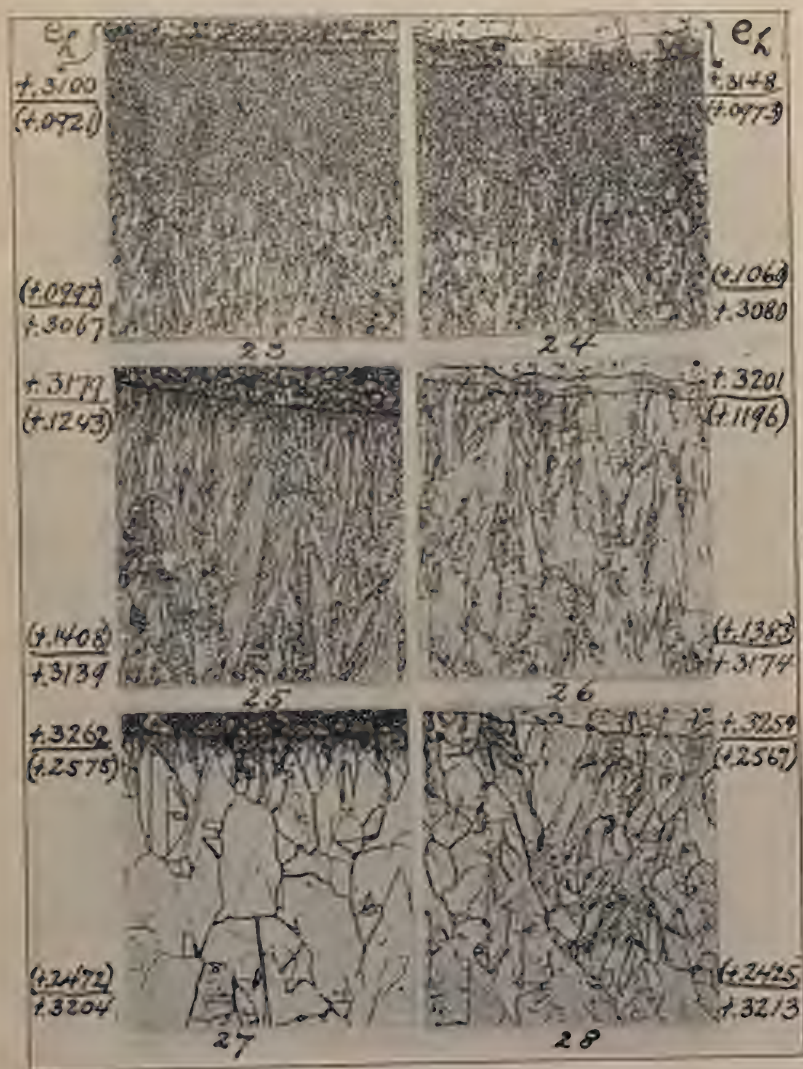


FIG. 8. Effect of Temperature.
 $\times 100$. Etched with $\text{NH}_4\text{OH} + \text{H}_2\text{O}_2$.

C. D. 3 amp./sq. dm.
 CuSO_4 1.5 N
 H_2SO_4 1.0 N

No. 23 and No. 24, 15° C.
 No. 25 and No. 26, 25° C.
 No. 27 and No. 28, 35° C.

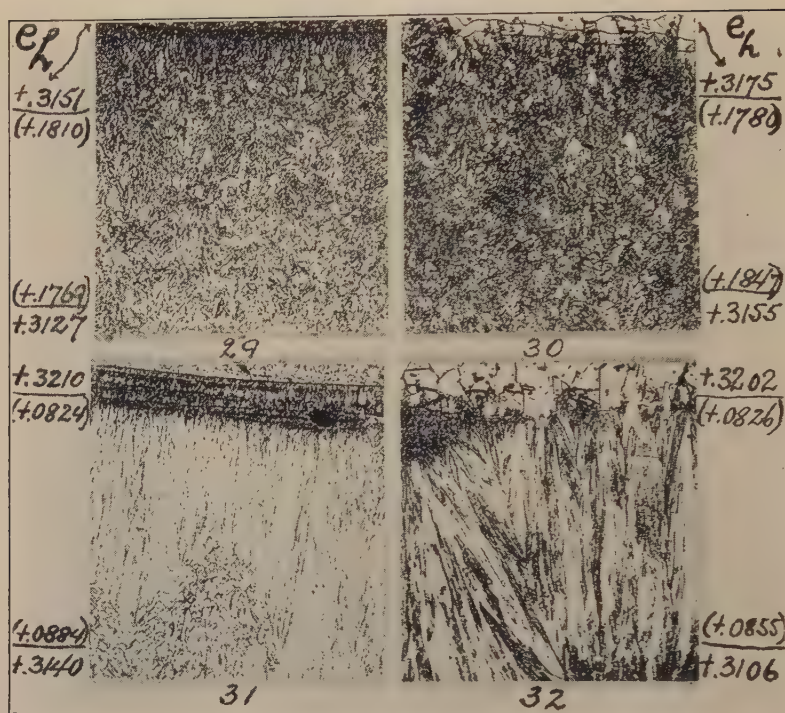


FIG. 9. Effect of Adding Gelatine.
x 100. Etched with $\text{NH}_4\text{OH} + \text{H}_2\text{O}_2$.

Temp. 25°C .
 CuSO_4 1.5 N
 H_2SO_4 1.5 N

No. 29 and No. 30, 3 amp./sq. dm.
No. 31 and No. 32, 3 amp./sq. dm.
with 0.02 g./L. gelatine

TABLE V.

Effect of Temperature on Cathode Polarization and Structure in Copper Deposition.

Standard conditions.

Fig. No.	Spec. No.	Variable: Temp. $^\circ \text{C}$.	Initial Cathode Polarization Volts	Structure
8	23	15	0.2179	Conical, twinned (fine)
8	25	25	0.1936	Conical, twinned (large)
8	27	35	0.0687	Conical (coarse)
8	24	15	0.2175	Conical, twinned (fine)
8	26	25	0.2005	Conical, twinned (large)
8	28	35	0.0687	Conical (coarse)

TABLE VI.

Effect of $Al_2(SO_4)_3 \cdot 16H_2O$ Addition on Cathode Polarization and Structure in Copper Deposition.

Standard conditions.

Fig. No.	Spec. No.	Variable: $Al_2(SO_4)_3 \cdot 16H_2O$		Initial Cathode Polarization Volts	Structure
		g./L.	oz./gal.		
6	15	...	...	0.1936	Conical, twinned
7	21	7.5	1.0	0.1818	Twinned, broken
6	16	...	...	0.2005	Conical, twinned
7	22	7.5	1.0	0.1810	Twinned, broken

TABLE VII.

Effect of Gelatin Addition on Cathode Polarization and Structure in Copper Deposition.

Standard conditions, except 1.5 N H_2SO_4 .

Fig. No.	Spec. No.	Variable: Gelatin		Initial Cathode Polarization Volts	Structure
		g./L.	oz./gal.		
9	29	...	...	0.1341	Broken (fine)
9	31	0.02	0.003	0.2386	Fibrous
9	30	...	...	0.1395	Broken (fine)
9	32	0.02	0.003	0.2376	Fibrous

centration of gelatine above which this takes place, since it stops very abruptly (See 31) after the concentration is reduced, and the amount remaining in solution continues to exert a marked influence on the structure of the deposited metal.

The influence of the base metal was slight in the electrolyte without the addition agent (See 29 and 30). With the addition agent, the structure of the deposit is coarser with the large grained base metal. (See 32.)

POTENTIAL READINGS.

The static potential values in Fig. 4 to 9 became less noble in each case after plating. The slight difference can most readily be explained by the roughness of the electrodeposit.

The dynamic potentials (values in parentheses Fig. 4 to 9) with only few exceptions became more noble (polarization decreased) as the thickness of the deposit increased, the difference between the beginning and end being so small that the practice of taking such measurements during the progress of deposition was abandoned after the first few runs. This decrease in polarization can partly be explained by the fact that as the electrodeposit increased in thickness, the area of the cathode also increased, and the current density would of course decrease somewhat.

While Blum and Kohlschütter, as already mentioned, attempt to explain differences in structure of electrodeposits by differences in the cathode potential or polarization, the writer does not offer any conclusion of this nature. It is to be noted from the potential tables and figures that a decrease in polarization of only 0.01 to 0.02 of a volt on the addition of aluminum sulfate produced a marked change in structure, but a decrease of 0.05 of a volt on doubling the copper concentration does not produce a change of the same degree. On the other hand, an increase in temperature from 15° to 25° C. only caused a decrease in polarization of about 0.03 of a volt, and yet the difference in structure can in no way be compared to that obtained in the two previous cases where the polarization changes were of the same magnitude.

One other case should be cited. A 100 per cent increase in acid concentration increased the polarization about 0.1 of a volt. A 200 per cent increase in acid concentration increased the polarization only about 0.04 of a volt.

In view of these facts any generalization on the relation of cathode polarization to the structure of the electrodeposited metal, based upon the contents of this paper alone, would be open to criticism similar to that already offered by Hughes, Blum and the writer in the opening paragraph.

SUMMARY.

1. A simple device for maintaining a constant solution level is described.
2. A new design of calomel electrode for preventing diffusion of potassium chloride into an electrolyte is described.

3. Additional confirmation of the evidence that the base metal influences the structure of electrodeposited copper is offered.

4. The effect of the variables influencing the structure of electrodeposited metal have been studied under uniform conditions.

5. Cathode potential measurements are given as data, which, it is hoped, will assist in offering some explanation of the relation of polarization to the structure of deposits, as more work of this nature is done.

ACKNOWLEDGMENT.

The author is deeply indebted to Dr. Hiram S. Lukens, to whom he wishes to express his sincere thanks, for directing this work and for the encouragement rendered. He also wishes to thank Mr. Wm. H. Bassett of the American Brass Company for furnishing the copper used, Dr. E. P. Polushkin, of Columbia University, for assistance with the photomicrographs and Dr. Wm. Blum for discussing the results of the paper with him.

